

SUMMARY REPORT

THE DEVELOPMENT OF DISPERSION-STRENGTHENED  
NICKEL CHROMIUM OXIDATION RESISTANT ALLOYS

E-3806

by

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prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

July 11, 1966

CONTRACT NAS 3-7279

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Abstract

Ilikon Corporation had developed a method of stabilizing certain dispersed phases in a metal matrix which Ilikon calls STAP (STabilized Precipitate). Using this method, an alloy containing 2-8 volume percent of aluminum-titanium oxide with a particle size of less than 0.1 micron and a particle spacing of about 0.3 to 1 micron was to be prepared from -325 mesh powder of a nickel base alloy containing 20.3 weight percent chromium and 3.2 weight percent titanium plus aluminum in a weight ratio of approximately 1:1. In this alloy the specified distribution was not produced throughout the alloy with any consistency with the standard STAP treatments employed. A coarse oxide appeared on the surface of the individual powder particles. This should be prevented or removed by suitable process control or by a cleaning technique.

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## THE DEVELOPMENT OF DISPERSION-STRENGTHENED

### NICKEL CHROMIUM OXIDATION RESISTANT ALLOYS

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#### SUMMARY

This is a summary report which covers Task I of an initially projected three task program. The over-all objectives of this program were to develop and evaluate nickel base alloys, dispersion-strengthened by aluminum oxide or by aluminum oxide plus titanium oxide, with the goal of producing material having a 3000 hour stress rupture strength of 15,000 psi at 2000°F. The objective of Task I was to develop the process variables to produce a specified dispersion strengthened alloy by using a technique which produces an oxide dispersion alloy in which the characteristics of the dispersed phase do not change, that is, the dispersed phase does not change in size or distribution or redissolve at elevated temperatures. This technique was previously developed by Ilikon Corporation (1)\* and called STAP, which is an acronym for STabilized Precipitate. In this process a precipitate is formed in certain alloys of the so-called precipitation hardening type. By introducing oxygen into the alloy, certain components related to the precipitate can be oxidized, thereby stabilizing the precipitate or preventing the precipitate from changing its characteristics (1).

The specifications for the proposed alloy were given as follows: it should contain 2-8 volume percent of stable oxides homogeneously distributed in a matrix composed of 15-30 weight percent of chromium, a small amount of titanium and aluminum, and the balance nickel. The oxide was to have an average particle size of less than 1000Å (0.1μ) and an average interparticle spacing of less than 10,000Å (1μ). For the purpose of Task I, an alloy of at least 90% theoretical density was to be produced. Task II was to utilize the process developed under Task I to produce seven billets of different compositions, and Task III was to evaluate three of the seven billets produced in Task II. The program was not taken into Tasks II and III.

Of the several alloy compositions investigated, an alloy containing 20.3 weight percent chromium and about 3.2 weight percent of titanium plus aluminum in a ratio of a little less than 1:1 with

\* Numbers in parentheses indicate references at the end of the text.

the balance nickel showed the most promise with regard to responding to the particle stabilizing treatment. All material was in powder form, minus 325 mesh, produced by argon atomization. The aging treatment conditions that produced particles within the program guidelines were 48 hours or more at temperatures above 750°C. The possibility of producing an alloy containing 2 to 8 volume percent of a stable oxide with an interparticle spacing of 0.3 to 1  $\mu$  and a particle size range of 0.1 to 0.3  $\mu$  was confirmed but, in this specific alloy, and with the treatments utilized, difficulties were encountered in trying to reproduce this distribution consistently throughout the entire sample. (Appendix A shows calculations for obtaining the interparticle spacing range.)

In addition to the stabilization treatment, a program was set up to clean the powders to eliminate a coarse oxide which tended to appear in the interparticle boundaries. The use of a cleaning solution containing nitric and hydrofluoric acids in a 5:1 ratio at about 50°C indicated that this was a feasible operation.

All of the evaluations of particle size and distribution, as well as the distribution of the coarse oxide, were made by use of electron microscopy, optical metallography and X-ray methods.

## I. INTRODUCTION

The fact that a dispersed second-phase strengthens a crystalline matrix has long been recognized and made use of. A great majority of the commercially important engineering metal alloys derive their strength on this basis. Well-known examples include steels containing dispersions of cementite in a ferrite matrix, be they in the form of lamellar cementite in a pearlitic structure or of spheroidal cementite in a tempered martensitic structure. Precipitation-hardened ferrous and non-ferrous alloys demonstrate a marked strengthening effect due to the finely dispersed precipitate phase. The term "dispersion-strengthening" has, however, come to be applied to a specific type of dispersed second phase strengthened alloy. This type, of which SAP and, lately, TD nickel are the most important commercially available materials, usually contains as the dispersed phase an oxide which is stable with respect to the matrix at all temperatures up to the melting temperature of the matrix.

From consideration of yield strength and creep strength calculations (2), it can be shown that the most important factors determining the strength of two-phase alloys at elevated temperatures are:

- A. The second phase should be very finely and very evenly distributed.
- B. This fine distribution should be unchanged after prolonged exposure to the service temperature.
- C. The shear modulus of both the dispersed phase and the matrix should be high. (This is more important in the case of the dispersed phase.)
- D. The coefficient of self diffusion of the matrix should be small.
- E. A good bond should be formed between the matrix and the dispersed phase.

The first two of the above list of properties are by far the most important.

The most desirable way to obtain a very fine dispersion of one phase within a matrix of another phase is to precipitate the dispersed phase from a supersaturated solid solution (3). By careful choice of the composition and of the aging time and aging temperature it is possible to control the formation of the precipitated phase so that a large number of small, closely spaced and uniform particles of the precipitated phase are formed. If these particles can then be stabilized, that is, treated in such a way

as to prevent them from changing in size or distribution or from redissolving, the two major design requisites will have been met. It is for this purpose that this program was carried out.

The commercially available nickel base superalloys normally contain one or more of several different precipitates in order to give them high yield strengths (4). These precipitates are generally of the  $\gamma'$  phase form, or  $Ni_3(TiAl)$  or  $Ni_3Ti$ , or may possibly include a number of carbides or borides. The most common and best documented of these phases is the  $\gamma'$  and it is the formation and stabilization of these particles in a nickel-chromium matrix with which this program was concerned. A typical alloy composition would be:

Nickel:	76 weight percent
Chromium:	20 weight percent
Aluminum + Titanium:	4 weight percent

This is similar to that used in some of the early nickel-base superalloys, as, for example, Nimonic 80A.

The rate of growth of the  $\gamma'$  particles in a Ni-Cr-Ti-Al alloy has been studied in the past (5). A schematic representation of particle size vs. aging time is shown in Figure 1. The most interesting feature of this curve is the "long plateau region" in which virtually no increase in particle size occurs with increasing aging time. It is in this region that the stabilization of the second phase particles can be carried out.

If, after formation of the precipitate, the alloy is exposed to a partial pressure of oxygen which is great enough to oxidize the titanium and aluminum but which is not great enough to oxidize the nickel or chromium, then the oxygen will diffuse through the alloy matrix and oxidize the precipitated particles. By proper design of the alloy, the stabilization and precipitation temperatures will be the same and the stabilization will be complete before the particle size/time curves start to rise again.

The composition of the oxidization product formed will depend on the composition of the alloy; it could be  $Al_2O_3$  or  $TiO_2$ , which have excellent solubility, or some more complicated mixed oxide (possibly containing Ni or Cr) such as a spinel. In this way an alloy which has a particle distribution that is the same as that of the precipitation strengthened superalloy is formed; in the context of this report we have chosen to describe this as a stabilized alloy or one in which the precipitated phase has been stabilized. The stability of a precipitated phase produced in this manner has been found to be excellent. It would be expected that the oxides formed will also have the high shear modulus which is necessary on the basis of yield strength calculations.

## II. PRIOR HISTORY

Research at Ilikon in the early 1960's (1,5,6) showed that it was possible to treat certain Ni-Cr-Ti-Al alloys so as to obtain and maintain a predetermined distribution of fine oxide particles. Such alloys were said to be stabilized. These alloys normally would form a solid solution when annealed above 1000°C and would precipitate out a finely dispersed  $\gamma'$  [Ni<sub>3</sub>(TiAl)] phase when subsequently aged at temperatures in the range 600-800°C.

When powders of these alloys are so aged and then exposed to an oxidizing atmosphere, such as that generated by a nickel/nickel oxide mixture, Ilikon found (by X-ray, electron micrography, and hardness studies) that a stable oxide precipitate phase was formed. This proprietary process, called STAP (STabilized Precipitate), combines the best attributes of the second phase distribution produced by solid state precipitation reactions with the thermal stability associated with the use of an insoluble non-diffusible second phase as normally used in conventional dispersion strengthening (1).

In these early treatments carried out at Ilikon, water atomized powders containing approximately 20 percent chromium, 4 to 5 percent titanium plus aluminum, and the balance nickel, were aged at 750°C for 20 to 48 hours in the presence of the atmosphere generated by a 1:8 nickel - nickel oxide mixture held at temperature. After consolidation and solid solution treatment of the powder, the resulting ingot was found to contain very fine oxide particles (300 to 500Å) which were uniform in size and distribution. The size and distribution, in fact, closely resembled that of the  $\gamma'$  phase which would have been formed if the alloy had been treated in the absence of an oxidizing atmosphere. Investigation of the thermal stability at 2300°F of this fine oxide showed that it did not redissolve in over 8 hours (1,6).

These alloys contained an undesirable amount of contaminant, in the form of a coarse surface oxide, which would have a weakening effect at high temperatures. To control this contaminant, a program was designed to investigate the amount and source of oxygen available during stabilization; the powder was exposed for 48 hours at 750°C in a continuously pumped high vacuum chamber prior to being compacted and examined. Since the structure observed after the vacuum treatment was the same as that observed after oxygen treatments, this seemed to indicate that the surface of the powder might be a source of an excessive supply of oxygen. Therefore argon atomized powder, which would have a much cleaner surface, was recommended for future work.

### III. EXPERIMENTAL INVESTIGATION (PROCEDURES, OBSERVATIONS & RESULTS)

#### A. Background

The first aspect of the research program examined under this contract was the control of the dispersed phase at a preselected level within the range 2-8 volume percent. It was intended that this control would be exercised by varying the  $\gamma'$  particle distribution since the prior, unpublished work at Ilikon indicated that the distribution of the stabilized phase appeared to be influenced by that of the  $\gamma'$  phase. This distribution can be controlled by varying either the composition of the starting powder or the stabilizing treatment conditions (time and temperature) or both. However, since the time and temperature also affect the stabilization process, it was decided that control over the oxide particle distribution would have to be exercised by varying the powder composition.

In the previously mentioned studies carried out at Ilikon (1) one composition (74-75 percent nickel, 20 percent chromium, 3.5 percent titanium, and 1.9 percent aluminum) which had been studied in detail was found to give particle contents in the upper half of the range 2-8 volume percent. A reduction in the titanium plus aluminum content of the starting powder would be expected to give a reduction in the volume percent of  $\gamma'$  phase present which, after stabilization, would give a reduction in the volume percent of stabilized particles in the STAP treated alloy. However, reducing the titanium-aluminum content by too great an amount would give an alloy which would not form a  $\gamma'$  precipitate under the treatment conditions. A study was conducted, therefore, to determine the range of titanium plus aluminum content which would give  $\gamma'$  precipitates, and which would, on stabilization, give the desired particle distribution within the range 2-8 volume percent.

This study was carried out on cast specimens rather than on powders because of the greater ease of production and handling of the cast material. A number of nickel-chromium-aluminum alloys were studied in addition to nickel-chromium-titanium-aluminum alloys because it was intended to study the stabilization of both of these series of alloys later in Task II and from this the best powder composition was to be selected.

#### B. The Formation of the $\gamma'$ Precipitate in Cast Alloys

##### 1. Procedures

The cast alloys were melted using the furnace system shown in Figure 2. The composition of these alloys is shown in Table I. The starting materials were:

- $\frac{1}{2}$ -inch diameter nickel rod (99.95% pure)
- Chromium platelets (99.95% pure)
- Titanium sponge (99.7% pure)
- Aluminum ingots (99.99% pure)



Prior to being weighed out, the nickel rod and aluminum ingots were cut into pieces with maximum dimensions of one inch and these pieces were chemically cleaned. The titanium and chromium were used in the as received condition. The pre-determined weight of each element was placed into a hafnia-stabilized zirconia crucible. These crucibles were used because of their inertness to attack by alloys of the compositions being studied. The crucible was transferred to the induction furnace system (Figure 2) which was then evacuated. After a subsequent flushing with high purity argon, the furnace was re-evacuated and the temperature raised to a few hundred degrees centigrade while pumping was continued. This treatment allowed degassing of the system. At a temperature below red heat (and below the melting point of aluminum) the pumping was stopped and approximately two-thirds of an atmosphere of high purity argon was introduced into the furnace system. The purpose of the argon was to reduce the rate of evaporation of the elements when they eventually became molten. The temperature of the charge was then raised to give complete melting of all four components. Adequate mixing of the elements was achieved by the stirring effect of the eddy currents induced in the molten charge during induction heating. The melt was allowed to solidify in situ in the furnace.

The ingots produced by the process described herein were cooled to room temperature and then removed from the zirconia crucibles. The outer surfaces of these ingots were ground to remove what was presumed to be a thin oxide skin which formed during heating. The ingots were homogenized between 1100°C and 1300°C for 2 to 16 hours in an inert atmosphere of argon or hydrogen or, in some cases, in vacuum. Hardness and metallographic examination indicated that the resulting material was homogeneous. These ingots were used to study the formation of the  $\gamma'$  phase.

The cast and homogenized ingots were cut up into specimens of approximately 1/2" x 1/4" x 3/4" and these pieces were solid solution annealed for two hours at 1100°C and water quenched. Aging of the specimens was carried out in either vacuum or an argon or hydrogen atmosphere in a furnace of the type shown in Figure 3. The specimen to be aged was kept in a nickel boat in the cold zone of the furnace while the hot zone was raised to the aging temperature and allowed to come to equilibrium. The nickel boat and the specimen were then placed in the hot zone, where they were held for the required aging period, after which they were returned to the cold zone. Whenever possible, specimens of more than one composition were aged simultaneously.

The aged specimens were ground flat on both larger faces and Rockwell hardness was measured. One surface was then polished down to a 9  $\mu$  diamond finish, followed by electropolishing in a mixture containing:

450 cc	Acetic Acid
40 cc	Perchloric Acid
15 cc	Water

The surface obtained was suitable for observation by replication electron microscopy. Germanium shadowed mowital replicas were used. Not all specimens were replicated. If the hardness measurements showed no change as compared with the solid solution treated material it was assumed that no  $\gamma'$  phase had been formed. In all cases where this assumption was checked by electron microscopy it was found to be correct. Data is shown in Table I.

## 2. Observations and Conclusions

From the studies on cast materials it was found that for (Ti + Al) contents of less than 2.3 weight percent no formation of the  $\gamma'$  phase was detected, while for (Ti + Al) contents greater than 2.6 weight percent the presence of the  $\gamma'$  phase was always detected by both electron microscopy and by its effect on hardness. Both the size and the volume percent of the  $\gamma'$  particles appeared to increase rapidly with increasing titanium plus aluminum content (see Figures 4-6). Above 5 weight percent, considerable coarsening of the  $\gamma'$  particles occurred.

In the limited compositions studied, the ratio of Ti:Al was not observed to have any appreciable effect on the size or distribution of the  $\gamma'$  phase produced after short aging times less than 24 hours. However, it was observed that the alloys with titanium contents greater than 1.75 percent but within a 2:1 titanium:aluminum ratio were more likely to show overaging on annealing for more than 48 hours at 750°C. The relationship between  $\gamma'$  particle size and aging time at 750°C has been discussed before (4) (Figure 1). The existence of the plateau in this curve was of importance because it is within this time that the stabilization must be carried out. From previous studies, it was known that between 20 and 48 hours were needed at 750°C in order to stabilize -325 mesh powders all the way through. The plateau region should therefore be at least 48 hours long. In only one alloy, nickel - 77.4; chromium - 20; titanium - 1.75; aluminum - 0.85, was any increase in particle size (and the related decrease in hardness) observed within 48 hours. Prolonged (100 hour) anneals of the other alloys, however, confirmed that the titanium rich alloys showed overaging more rapidly than the aluminum rich alloys with the same total titanium plus aluminum content (see Table I). This study of the  $\gamma'$  phase formation allowed us to choose the powder compositions described in the following sections.

### C. Initial Stabilization Treatments

#### 1. Material

For use in the initial STAP treatments, an argon atomized alloy composition containing 19.4 percent chromium, 1.08 percent titanium, 1.82 percent aluminum, and the balance nickel, was ordered

in the form of -325 mesh powder. Table II shows the composition of the alloys ordered by both specification and vendor analysis. The powder was produced by Hoaganaes Sponge Iron Co. and argon atomization was specified, as discussed in Section II previously, because of the resulting lower oxide content as compared to water atomized powders. The reasons for obtaining this particular composition were:

- a. Previously treated powders gave oxide contents upwards of 2-8 volume percent in alloys containing 4-5 weight percent of titanium and aluminum. In order to reduce the oxide content to the lower end of the 2-8 volume percent range, it was decided to reduce the titanium plus aluminum content to the minimum which had been shown by the studies on cast materials to be 2.6 weight percent.
- b. The most accurate compositional limits which the powder manufacturer would guarantee were:  
aluminum  $\pm 0.1\%$  of total alloy weight,  
titanium  $\pm 0.2\%$  of total alloy weight.
- c. For titanium plus aluminum contents at the lower end of the  $\gamma'$  precipitate producing range, it was found necessary to have an aluminum:titanium ratio greater than 1 in order to obtain maximum stability of the  $\gamma'$  phase. An alloy containing 2.9 weight percent titanium plus aluminum was chosen with a 2:1 aluminum:titanium ratio.
- d. A 4:1 nickel:chromium ratio was necessary to give oxidization resistance to the matrix.

## 2. Procedures

This powder was first treated in a continuously pumped vacuum system. Since early studies with water atomized powders indicated that sufficient oxygen was associated with the powder to act as the oxygen source for stabilization, it was assumed that this would still be true for the argon atomized material. The furnace system used for these treatments is shown in Figure 7. It contained a tantalum resistance furnace which was wound onto a quartz tube. Inside of the quartz tube was a stainless steel container (Figure 8) which contained the powders and which was rotated continuously to prevent sintering of the powders.

The following procedure was used with each batch of powder treated in this equipment:

- a. Approximately 350 grams of as-received -325 mesh powder was charged into the stainless steel container. The container was mounted inside the vacuum chamber and evacuated to  $< 1 \times 10^{-8}$  torr.
- b. The powder temperature was raised to  $250^{\circ}\text{C}$ , and pumping was continued to maintain a pressure below  $1 \times 10^{-8}$  torr.
- c. This procedure was repeated at  $400^{\circ}\text{C}$  and again at  $600^{\circ}\text{C}$ , after which the temperature was raised to the treatment temperature and maintained for the required time; the powder was furnace cooled.
- d. After treatment, the vacuum chamber was purged with high purity nitrogen and the stainless steel container was transferred to a dry box where the treated powder was removed from the container and placed in a graphite mold. The material was then hot pressed at  $1200^{\circ}\text{C}$  and 2000 psi in the mold in an induction furnace (Figure 9) with a resulting ingot density of 80%.
- e. The surface of the pressed ingot was then ground to remove contaminants. The cleaned ingot was next sealed in an evacuated stainless steel shell and forged at  $1200^{\circ}\text{C}$  to give a 50% reduction in height. The forged ingot was decanned, cleaned, annealed in vacuum (or, in some cases, dry hydrogen) for at least two hours at  $1200^{\circ}\text{C}$ , and water quenched. This treatment was intended to redissolve any unstabilized  $\gamma'$  particles which might have existed. Stabilized oxide particles should not be affected by the treatment.

Three treatments were carried out in the ultrahigh vacuum system. These were at treatment temperatures of  $700^{\circ}\text{C}$ ,  $750^{\circ}\text{C}$ , and  $780^{\circ}\text{C}$ , and each was for 48 hours.

### 3. Observations and Conclusions

The structure of the ingot was examined by electron microscopy using two stage carbon replicas. The electron microscopic examination of these materials showed that stabilization had not occurred. The only second phase material observed was confined to the boundaries between the original powder particles. It was found that this oxide was much more prevalent at the exterior of the ingots than in the interior, and it was concluded that the observed oxidization had occurred during the compaction of the STAP treated powders rather than during the STAP treatment of these powders. It was therefore concluded that there was not enough oxygen present to give stabilization of the  $\gamma'$  phase. A new series of treatments in which more oxygen would be available was planned.

## D. Intermediate Series of Treatments

### 1. Material

The powder used was from the same batch as that used in the initial stabilization treatments described in Section C.

### 2. Procedures

The intermediate series of treatments were carried out in atmospheres which should act as an oxygen supply to the nickel-chromium-titanium-aluminum powder being treated. These treatments were carried out in a quartz tube furnace of the type shown in Figures 10 and 11. The powder was contained in stainless steel containers of the type shown in Figure 12 and, as in the ultrahigh vacuum system, the powder was rotated continuously.

In the first treatment, 150 grams of as-received powder was placed in each end of the stainless steel container (Figure 12). The container was placed in the furnace and the temperature was raised to 750°C. The system was pumped continuously to maintain a vacuum of approximately  $1 \times 10^{-5}$  torr. After 48 hours at temperature, the powder was consolidated as described earlier.

In the next series of treatments, oxygen was deliberately introduced into the system by placing a 1:8 mixture of a nickel - nickel oxide powder in one half of the stainless steel container while the other half was filled with 150 grams of atomized powder for treatment. The two halves of the container were physically separated by a partition. In this way the nickel-chromium-titanium-aluminum powder was subjected to the partial pressure of oxygen which exists in equilibrium with the metal/metal oxide mixture at the temperature of the powder treatment. The treatment conditions are listed in Table III. Two additional treatments were carried out in an atmosphere generated by a 1:8 Mn/MnO<sub>2</sub> mixture (see Table III). The purpose of these treatments was to see if there was an effect due to a different oxygen partial pressure as generated by this mixture.

The procedure used during this series of treatments follows:

- a. The nickel-chromium-titanium-aluminum powder charge was put into one end of the stainless container and the metal/metal oxide mixture was put into the other end.
- b. The container was placed in a furnace, evacuated to  $< 2 \times 10^{-5}$  torr, and rotated while the furnace temperature was raised to the treatment temperature.
- c. After treatment, the powders were hot pressed, forged and solid solution treated, as described previously.

### 3. Observations and Conclusions

The structure observed in the powder which had been treated under the  $10^{-5}$  vacuum was similar to that observed under the  $10^{-8}$  vacuum. In neither case did stabilized particles exist. Examination of the structures obtained by the treatments carried out in the presence of a metal/metal oxide mixture, however, showed that stabilization of the powder particles had occurred. Two types of oxide existed. A fairly coarse oxide was associated with the powder particle interfaces and a finer ( $.1\mu - .3\mu$ ) oxide was distributed within the powder particles (Figure 13). The amount of oxide within the particles was quite low however ( $\approx 2$  volume percent). Comparison of the structures obtained using the nickel/nickel oxide mixture for the different conditions listed in Table III showed that a slight increase in volume percent of oxide did occur when longer times of exposure were used. No appreciable variation could, however, be detected between the  $750^{\circ}\text{C}$  and  $780^{\circ}\text{C}$  treatments. The Mn/MnO treatments appeared to give larger particles but the analysis was inconclusive. It was, however, decided to use a nickel/nickel oxide mixture in future stabilization treatments.

#### E. Final Series of Treatments

##### 1. Materials

Analysis of the intermediate series of treatments showed that powders of the type used could be stabilized. A third series of treatments was then carried out in order to try to obtain the required structures. Two paths were followed. One was to study the effect of powder composition by using other nickel-chromium-titanium-aluminum compositions, and the second was to extend the range of conditions under which the treatments were carried out.

Three new batches of -325 mesh, argon atomized powders were ordered to determine the effect of a modification of composition. The ordered and received compositions are listed in Table IV. The three compositions ordered were selected so as to be compatible with prior Task I work (Alloy I), to compare with Ilikon early work (Alloy II) and to reverse the Al:Ti ratio of Alloy II (Alloy III). It should be noted that in Alloy III there is a large discrepancy in the aluminum content between the ordered composition and the actual composition. A 1:8 nickel - nickel oxide mixture was used as an oxygen source in all treatments.

##### 2. Procedures

The STAP treatment procedures were the same as had been used in the intermediate series of treatments. In some cases it

was observed that the nickel - nickel oxide mixture was completely reduced to nickel during the STAP treatment and for this reason some treatments were repeated with an excess of nickel - nickel oxide. The treatments on these new powders were as follows:

24 hours at 750°C  
48 hours at 700°C  
48 hours at 750°C  
48 hours at 800°C  
48 hours at 850°C

and repeats of the above with a large excess of nickel oxide/nickel. Table V describes these treatments in greater detail.

### 3. Observations and Conclusions

With the final powders (Table IV), the 700°C/48 hour and 750°C/24 hour treatments produced very similar structures (Figure 14) for all three powder compositions. Particle formation occurred at the exterior of the powder particles but not in the interior. In the 750°C/48 hour and 800°C/48 hour treatments, stabilization as well as external oxidization of the powder particles did occur. The stabilized particles appeared to be associated with some form of grain boundary within the powder particles (Figure 15) but the distribution was not uniform. The average size of the particles produced in these regions was, in general, in the range .1 to .3 $\mu$ . The volume percent of stabilized particles present was at the lower end of the range 2-8 percent. A size analysis of the stabilized particles (disregarding the grain boundary oxide) in Figure 15 yields results as noted above.

The 850°C treatments were made in an attempt to produce stabilized particles throughout the powders rather than only in boundaries within these powders. Very little difference was detected, however, in the second phase distribution as compared with the similar 800°C treatments.

The second change which was instituted was to increase the total amount of the nickel/nickel oxide mixture which was used as the oxygen supply. By increasing the total quantity of oxygen in the system, Ilikon personnel felt that the amount of second phase particles that become stable might be increased. This would be feasible if increasing the concentration of oxygen in the subgrain boundaries would cause more rapid diffusion of oxygen into the subgrain. Since diffusion rate is a function of the concentration gradient, this was a plausible approach.

It was found that increasing the amount of nickel - nickel oxide was partially successful in so far as it caused a band of particles

to be associated with the boundaries (Figure 16) rather than the single line previously observed (Figure 15). The average particle size was found to be in the same range as that previously observed ( $.1\mu - .3\mu$ ). The volume percent of second phase present was, however, at the upper half of the 2-8 volume percent range. Thus controlling the amount of oxygen available did exercise some control on the volume percent of the stabilized phase formed but did not appear to affect the surface oxide. The distribution of the second phase shown in Figures 13, 15 and 16 was not uniform within a given powder grain, however.

F. Separate Treatments to Obtain the  $\gamma'$  Phase and to Obtain Stabilization

$\gamma'$  The possibility of using consecutive rather than simultaneous particle precipitation and stabilization treatments was considered. In these treatments, the distribution of the  $\gamma'$  phase would be established before the powders were exposed to the stabilizing atmosphere. Before these were carried out, it was decided to examine the formation of the  $\gamma'$  phase in the three powders.

Samples of each of the three final batches of powder (Table IV) were hot pressed, forged and solid solution treated under the same conditions that had been used with the treated powder. These samples were then cut into several parts, one of which was examined in the solid solution treated state and the others after having subsequently received various aging treatments.

Optical metallography of these samples showed that those formed from alloy compositions I and II of Table IV had, in all cases, etched very non-uniformly. This behavior was found with several independent methods of surface preparation and etching. Approximately 20 percent of the powder particles of Alloy II and 10 percent of those of Alloy I appeared inhomogeneous. To check if this structure was a result of any of the treatments which had been carried out on the powder, as-received powder was mounted in an epoxy resin and prepared for observation. The same structure was observed.

Examination of the  $\gamma'$  structure in samples of Alloy III which had been compacted, solid solution treated and aged showed that it was not identical to that which would have been expected to have been found in cast material which had received the same treatment. However, as noted earlier, the composition of Alloy III was found to be off considerably from the ordered composition and it fell below the guidelines for producing particles. The actual composition was not learned until after most of the experimental work had been completed. In the cast alloy, a uniform distribution of the type shown in Figure 4 would have been expected. In the compacted powder, however, there are a large number of boundaries within each particle and these boundaries appear to act as sites for the preci-



precipitation of the  $\gamma'$  phase (Figure 17). Although some  $\gamma'$  precipitation does occur within the area surrounded by these boundaries, the result is a non-uniform  $\gamma'$  structure with the formation of quite large particles in the boundaries - the structure is in fact very similar to the oxide structure obtained on the stabilization of this material. Basically, then, it was found that in the specific alloys used, and with the treatments described, particles could be stabilized but not so as to be uniform throughout the material.

#### G. Chemical Cleaning of Powders

In those cases in which the stabilized phase was formed within the powder particles, a coarse oxide was also observed to form on the surface of the powder particles. As it was not part of the desired dispersion, it was necessary to remove this coarse oxide. The procedure which was investigated is basically that of applying techniques normally used to pickle oxide from ingots of nickel base superalloys.

The powders were first sized by sieving to separate out any particles which may have sintered together during the stabilization treatment. The powder, all of which was -325 mesh, was then poured into a beaker containing a mixture of 16 parts  $H_2O$ , 5 parts  $HNO_3$  and 1 part  $HF$ . The temperature of this mixture was  $35-40^\circ C$  before the powder was added and it was maintained at between  $45^\circ C$  and  $50^\circ C$  during the cleaning process. The powder and cleaning solution were agitated together for several minutes and the cleaning solution was then decanted. The powder was subsequently washed with water and this process was repeated. The powder, which was a blue-black color after the stabilizing treatment, gradually turned grey. Observation of the grey powder showed it to consist of two types of particles, some of which were still blue-black and others of which were light grey. By decanting the grey powder with alcohol, it was possible to separate the residue into two fractions, one of which contained most of the blue-black material and the other of which contained most of the light grey material. The light grey powder was material which had been cleaned.

Cleaning was carried out primarily on powder of composition III which had been treated for 48 hours at  $750^\circ C$  in the presence of the increased amount of the nickel - nickel oxide mixture. The cleaned powders were compacted by hot pressing and hot forging prior to being observed by both optical and electron microscopy. It was found that a considerable decrease had occurred in the amount of coarse oxide present in the boundaries between the powder particles. Complete removal had not occurred, however. It should be pointed out that a complete cleaning program was not planned for Task I but was undertaken simultaneously to show the feasibility of the removal of the oxide so as to be able to eliminate it ultimately.

#### IV. RECOMMENDATIONS

The final structure developed in Task I differed from the target structure in two ways. A coarse oxide existed in some of the inter-powder particle boundaries, and a uniform distribution of stable particles could not be produced consistently in the alloy systems used with the standard treatments employed.

To determine compositional variables, studies were made on cast alloys early in Task I and the results were directly translated to powder materials. It was found, however, that structural data gathered from cast alloys could not be directly related to powders of the same composition. It became obvious during Task I that the distribution and quantity of the  $\gamma'$  phase could not be achieved in the powder form utilizing the treatments performed on the cast materials. Therefore it is recommended that preliminary studies to determine optimum alloy composition for STAP treatment be made with alloy powders rather than with cast samples.

It also may be well to look at the effect of composition limits resulting from variations in the homogeneity of the powders due to differences in manufacturing processes. Similarly the effect of argon atomized powders as compared with water atomized powders bears investigation.

There appears to be some doubt as to whether the argon quench is sufficiently rapid. In the event that it is not, then a full solution treatment is not achieved, uncontrolled precipitation can occur, and elements can become segregated within the alloy to such an extent that insufficient composition distribution exists to produce  $\gamma'$  (?). If this is the case, and if the stabilized particle morphology is dependent on that of the  $\gamma'$  (as has been shown in past work), then, since it is not possible to produce particles, there is nothing to be stabilized.

In the original studies to prepare STAP materials, powder consolidation was accomplished by extrusion; in Task I of this program forging was used in order to reduce costs.

The method of consolidation does, of course, influence the final distribution of the stabilized particles. Consequently, to achieve a more representative distribution, the treated powder should be extruded.

A more thorough study of chemical cleaning techniques for the elimination of the coarse oxide should be undertaken. Successful cleaning combined with extrusion would allow more latitude in the selection of powder manufacturing methods.

V. REFERENCES

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- (6) Bonis, L. J., New Approach to High Temperature Strength. Materials in Design Engineering, Vol. 58, No. 4, p. 104, October 1963.
- (7) Brandstedt, S. B., and Durdaller, C., Development of an Improved Manufacturing Process for the Production of Higher Purity Superalloy Powders. DDC Report No. AD 485-314, July 1966.

TABLE I

Cast Alloys, Composition, Hardness, and Treatment

Alloy Desig. <sup>1</sup>	Nominal Composition (%) <sup>3</sup>				Hardness Data <sup>2</sup>				Remarks
	Ni	Cr	Al	Ti	a	c	d	f	
A	80.58	14.22	5.20		R <sub>C</sub> 25	R <sub>C</sub> 26	R <sub>C</sub> 16	R <sub>C</sub> 26	Large coarse precipitate
B	78.8	17.26	3.94				R <sub>B</sub> 73	R <sub>C</sub> 20	Uniformly distributed precipitate 500 - 2000Å
C	74.95	20.88	4.17		R <sub>C</sub> 20	R <sub>C</sub> 38	R <sub>B</sub> 74	R <sub>C</sub> 22 R <sub>C</sub> 16	
D	70.2	25.9	3.9				R <sub>B</sub> 78		
F	78.7	17.4	2.4	1.5	R <sub>C</sub> 18		R <sub>B</sub> 65		
H	70.3	25.88	2.26	1.56	R <sub>C</sub> 14		R <sub>B</sub> 77	R <sub>C</sub> 23	
J	79.9	17.86	2.24		R <sub>B</sub> 52	R <sub>B</sub> 70	R <sub>B</sub> 63	R <sub>B</sub> 63	No precipitate
K	71.22	26.5	2.28		R <sub>B</sub> 62	R <sub>B</sub> 73	R <sub>B</sub> 64	R <sub>B</sub> 76 R <sub>B</sub> 58	
M	79	19.5	1.5		R <sub>B</sub> 58				
N	79	19.5	1	.5					
R	70	28	.5	1.5					
T	78	19	3		R <sub>B</sub> 91		R <sub>B</sub> 83	R <sub>B</sub> 91 R <sub>B</sub> 77	Uniformly distributed precipitate 300 - 1000Å
U	78	19	2	1	R <sub>B</sub> 74	R <sub>B</sub> 60	R <sub>B</sub> 84	R <sub>B</sub> 91	
W	78	19	1	2	R <sub>B</sub> 89		R <sub>B</sub> 93	R <sub>B</sub> 91 R <sub>B</sub> 68	
X	77.4	20	2.6		R <sub>B</sub> 62	R <sub>B</sub> 62	R <sub>B</sub> 84		
Y	77.4	20	1.75	.85	R <sub>B</sub> 88	R <sub>B</sub> 67	R <sub>B</sub> 91		
Z	77.4	20	.85	1.75	R <sub>B</sub> 73	R <sub>B</sub> 58	R <sub>B</sub> 68		

## Notes to Table I

Note 1 : Designations E, G, I, L, O, P, Q, S, and V not used.

- Note 2 :
- a) As cast.
  - b) Billet held at 1300°C for 16 hours and slowly cooled to room temperature.
  - c) As cast, then annealed 16 hours at 750°C.
  - d) As cast, then held at 1100°C for 2 hours and quenched.
  - e) As cast, held at 1100°C for 2 hours, quenched, and aged for 16 hours at 750°C.
  - f) As cast, held at 1100°C for 2 hours, quenched, and aged for 48 hours at 750°C.
  - g) As (b), held at 1200°C for 2 hours and quenched.
  - h) As (b), held at 1200°C for 2 hours, quenched, and aged 4 hours at 750°C.
  - i) As (b), held at 1200°C for 2 hours, quenched, aged at 750°C for 16 hours.
  - j) As (b), held at 1200°C for 2 hours, quenched, and aged at 750°C for 60 hours.
  - k) As cast, held at 1100°C for 2 hours, quenched, then aged 4 hours at 750°C.
  - l) As cast, rolled to  $\frac{1}{2}$  thickness, held at 1100°C for 2 hours, quenched, and aged 130 hours at 750°C.

Note 3 : Compositions were as prepared by weight. No chemical analysis was run.

TABLE II

Powder Composition for Initial Stabilization Treatments

	<u>Ni</u>	<u>Cr</u>	<u>Ti</u>	<u>Al</u>
Composition Ordered:	Bal.	19.4	1.08	1.82
Composition Received (by Analysis):	Bal.	19.4	1.12	1.94

TABLE IIIIntermediate Treatment Conditions to Achieve Stabilization

Atmosphere	Temperature	Time
Ni-NiO	750°C	24 hours
Ni-NiO	750°C	48 hours
Ni-NiO	750°C	72 hours
Ni-NiO	780°C	48 hours
Ni-NiO	780°C	72 hours
Mn-MnO <sub>2</sub>	750°C	48 hours
Mn-MnO <sub>2</sub>	800°C	48 hours

TABLE IV

Final Alloy Compositions

		<u>Ni</u>	<u>Cr</u>	<u>Ti</u>	<u>Al</u>
Alloy I	Composition Ordered:	Bal.	19.4	1.08	1.82
	Composition Received (by Analysis):	Bal.	18.8	1.01	1.96
Alloy II	Composition Ordered:	Bal.	20.0	2.92	1.45
	Composition Received (by Analysis):	Bal.	19.9	3.35	1.64
Alloy III	Composition Ordered:	Bal.	19.0	1.62	2.73
	Composition Received (by Analysis):	Bal.	20.32	1.53	1.71



TABLE V

Conditions and Results of Treatments on Final Alloy Powder Compositions  
in Various Atmospheres and at Various Temperatures

Spec. Desig.	Comp. (from Table IV)	Time (hr)	Temp. °C	Atmosphere Generated (a)	Results & Remarks (b)
A	I	48	750	Ni-NiO	Large subgrain particles
B	II	48	750	Ni-NiO	Large subgrain particles
C	III	48	750	Ni-NiO	Particles mainly in subgrain boundaries. Approximately 6 vol.% oxide with an average diameter of $.3\mu$ . (Disregarding grain boundary particles.)
D	I	48	700	Ni-NiO	
E	II	48	700	Ni-NiO	
F	III	48	700	Ni-NiO	
G	I	24	750	Ni-NiO	
H	II	24	750	Ni-NiO	Oxidation at particle faces
J	III	24	750	Ni-NiO	
K	I	48	800	Ni-NiO	Oxidation at particle faces
L	II	48	800	Ni-NiO	Oxidation at particle faces
M	III	48	800	Ni-NiO	
N	II	24	800	Cr <sub>2</sub> O <sub>3</sub>	
P	II	-	-	Ni-NiO	After undetermined time, thermocouple broke - no test
Q	I	-	-	Ni-NiO	After undetermined time, thermocouple broke - no test
R	I	-	-	-	Could possibly contain fine particles
S	II	-	-	-	Could possibly contain fine particles
T	III	-	-	-	Results inconclusive
U	I	48	750	Ni-NiO	Repeat of A with more Ni-NiO
V	II	48	750	Ni-NiO	Repeat of B with more Ni-NiO
W	I	48	850	Ni-NiO	
X	II	48	850	Ni-NiO	

Spec. Desig.	Comp. (from Table IV)	Time (hr)	Temp. °C	Atmosphere Generated (a)	Results & Remarks (b)
Y	II	48	750	NiO	Large quantity for powder cleaning
Z	III	48	750	Ni-NiO	Subgrain boundary oxidation. Ni-NiO placed in far end of can
AA	III	48	800	Ni-NiO	Ni-NiO placed in far end of can
BB	I	48	750	Ni-NiO	Grain boundary oxide. Ni-NiO placed in far end of can
CC	II	48	750	Ni-NiO	Ni-NiO placed in far end of hot zone of furnace
DD	1199 (c)	48	750	Ni-NiO	Ni-NiO placed in far end of hot zone of furnace
EE	I	48	750	Ni-NiO	Ni-NiO placed in far end of hot zone of furnace
FF	II	-	-	-	Pressed for aging studies
GG	III	48	750	NiO + old STAP	
HH	III	48	750	see remarks	Atmosphere was NiO + new STAP (pre-oxidized) + new STAP
JJ	III	48	750	Ni-NiO	
KK	III	96	750	Ni-NiO	
LL	III	see remarks	750	Ni-NiO	Pre-precipitated in vacuum at 750°C for 8 hrs., STAP treatment for 48 hrs.
MM	III	48	750	Ni-NiO	Powder pre-oxidized for 48 hrs. at 600°C
NN	1199 (c)	48	750	Ni-NiO	Small quantity Ni-NiO used
PP	III	48	750	Ni-NiO	Excess Ni-NiO used

NOTE: Specimen designations I and O not used.

(a) All metal-metal oxide mixtures were in a 1:8 ratio.

(b) Where no remarks are made either no particles appeared or, in a few cases, excessively large particles appeared.

(c) Alloy 1199 was one of the powders that Ilikon used prior to the NASA program - it contained 20.02 percent chromium, 1.02 percent aluminum and 2.92 percent titanium. The powders had been made by water atomization (which was the reason for its use here).

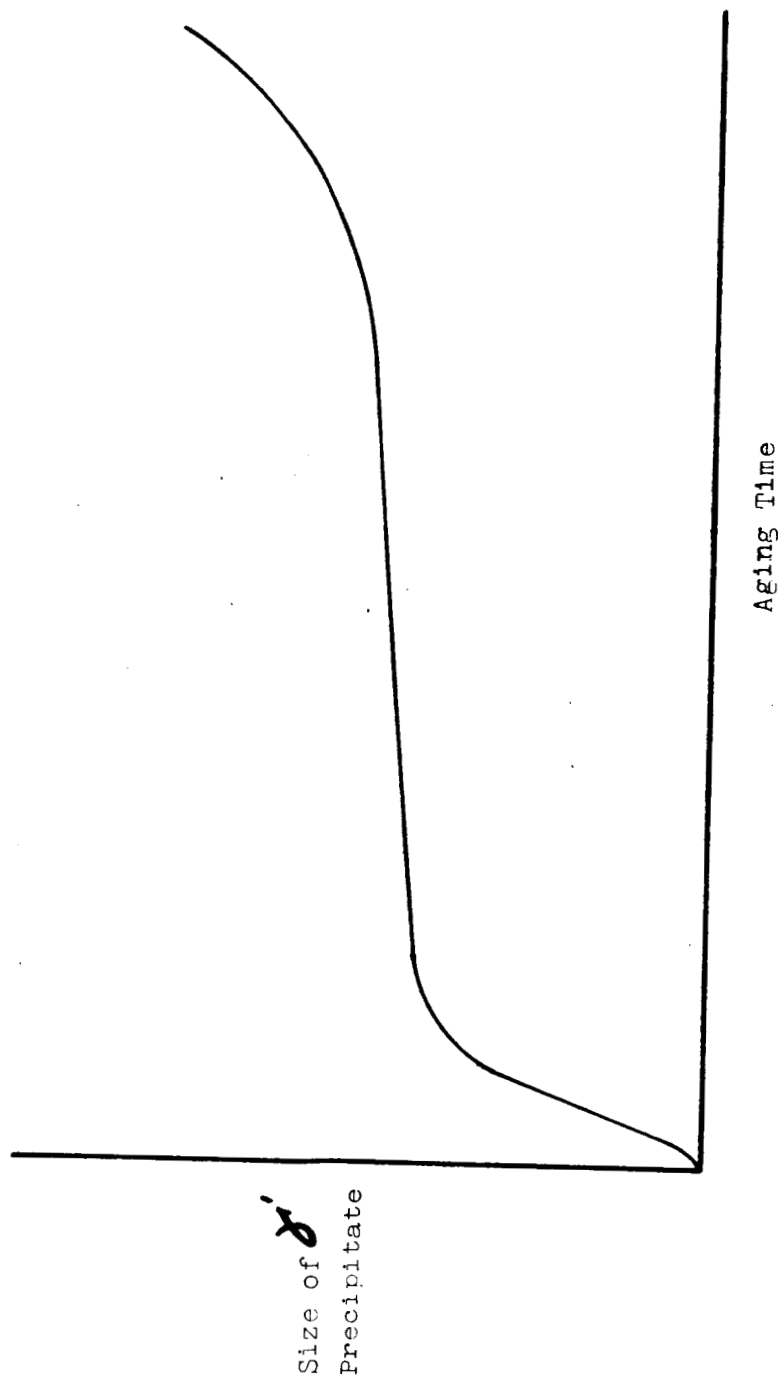


Figure 1 A schematic representation of the variation of  $r$  particle size with aging time.

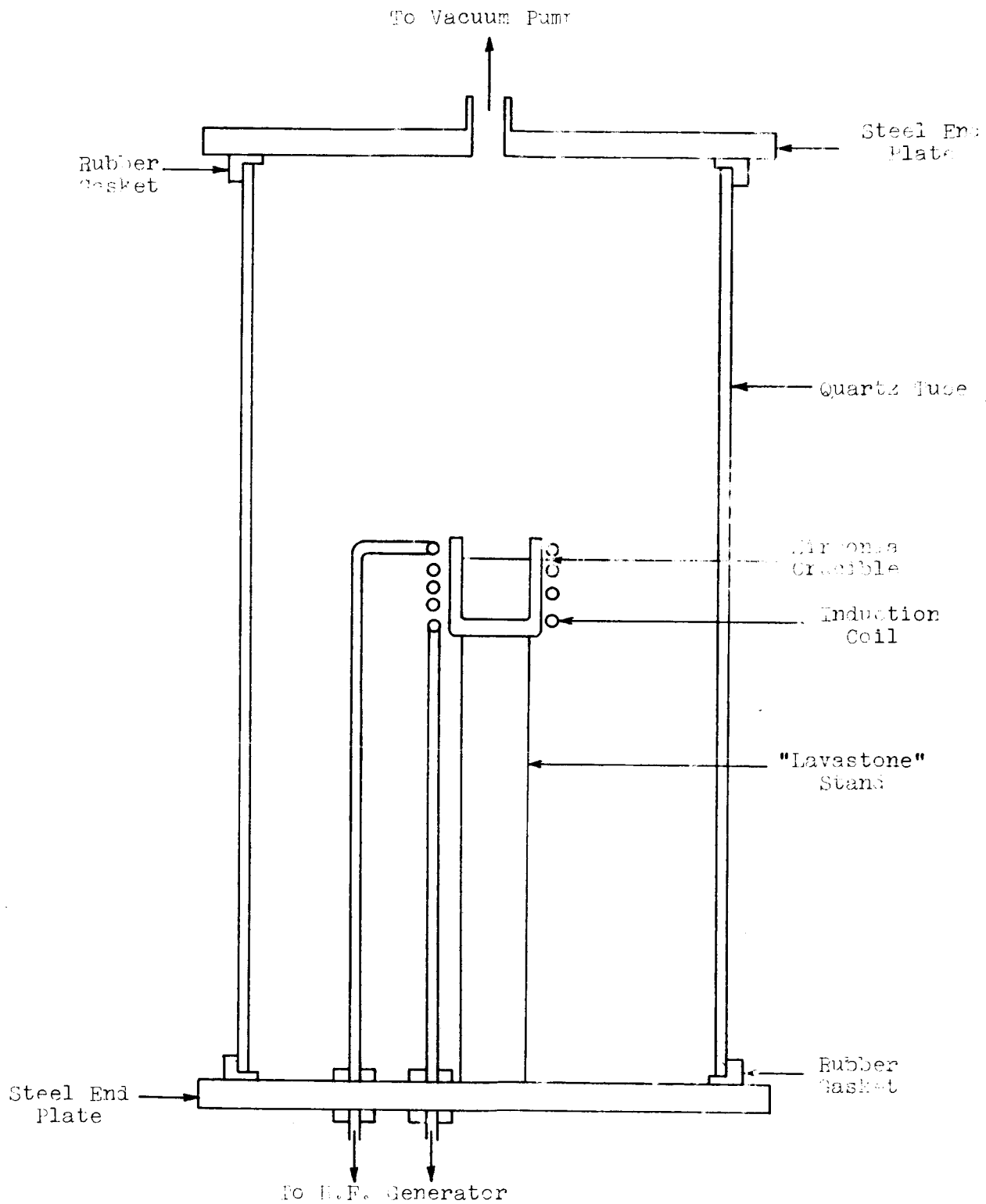


Figure 2 Furnace arrangement for casting specimens.

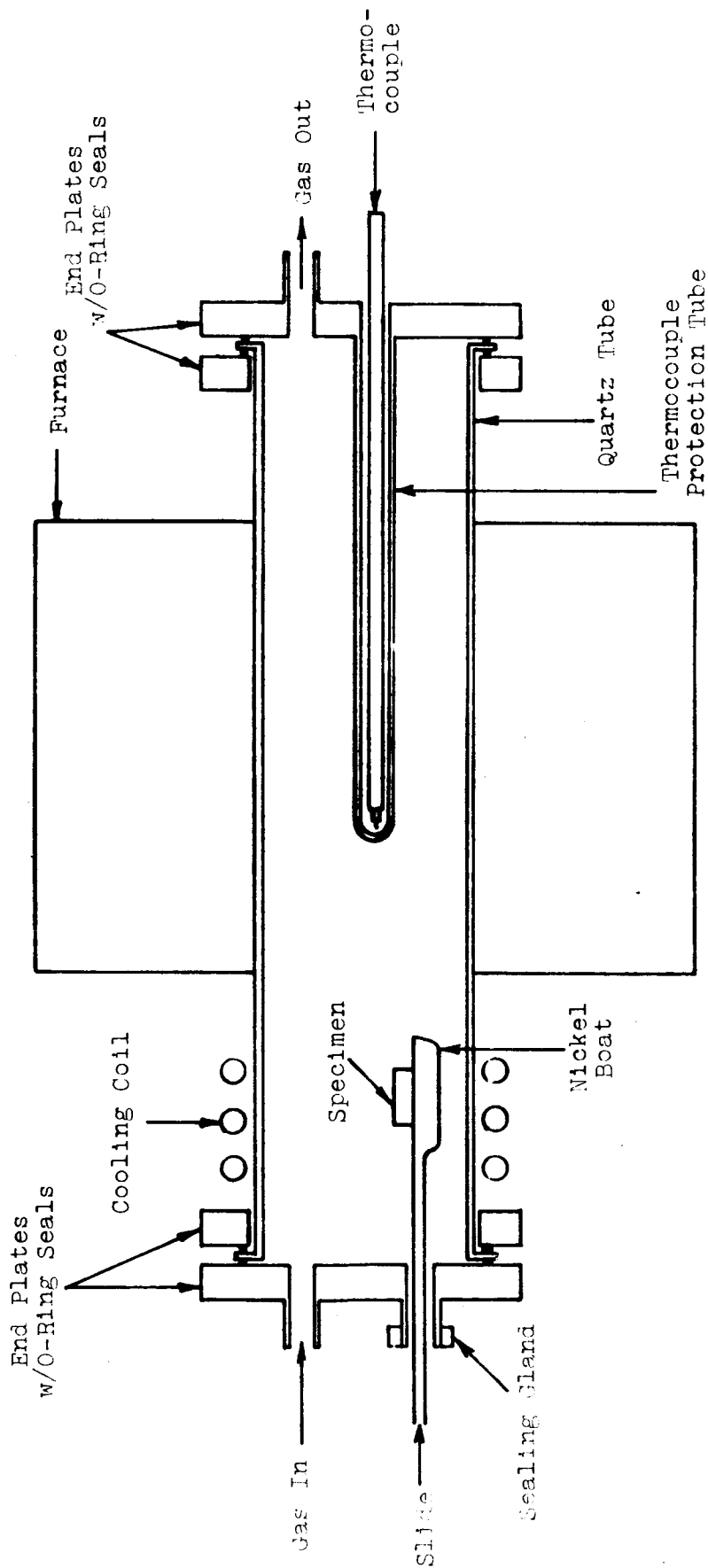


Figure 2

Aging furnace arrangement.



Figure 4

Electron micrograph of  $\gamma'$  particle formation  
in alloy W containing 3 wt.% (Ti + Al) and  
aged at 750°C for 16 hours. Ge shadowed  
Mowital replica. 20,000X

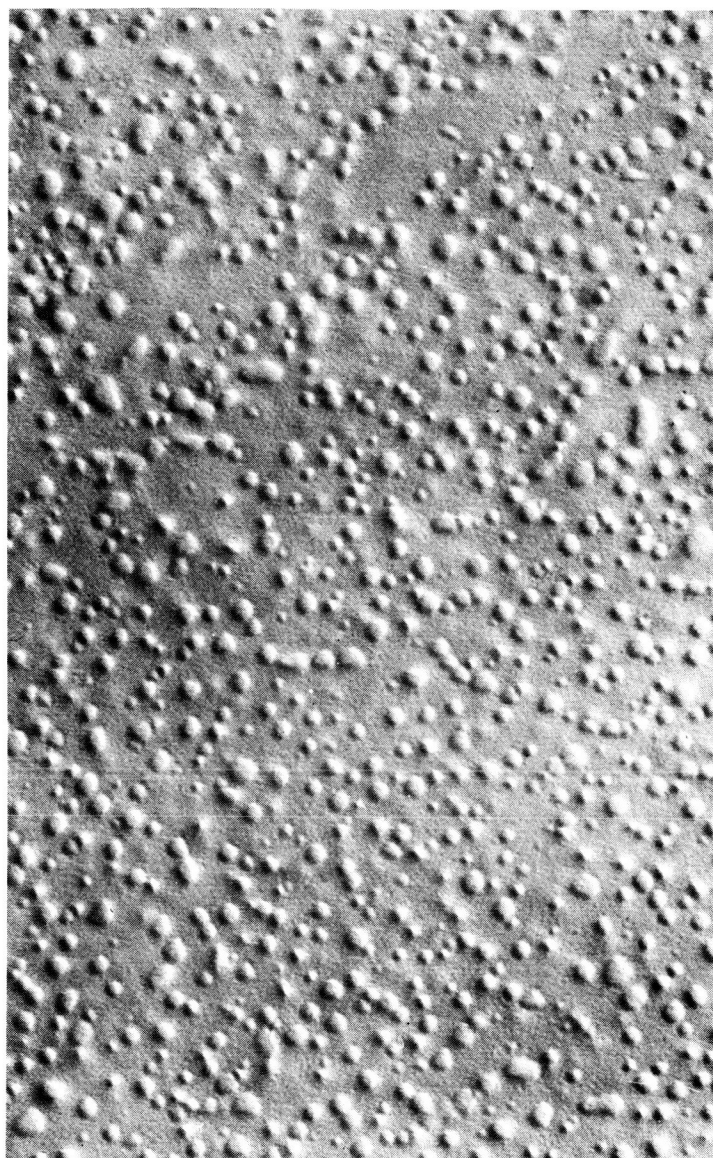


Figure 5

Electron micrograph of  $\gamma'$  particle formation in alloy C containing 4.17 wt.% Al and aged at 750°C for 4 hours. Ge shadowed Mowital replica. 20,000X



Figure 6

Electron micrograph of  $\delta'$  particle formation  
in alloy A containing 5.2 wt.% Al and aged at  
750°C for 4 hours. Ge shadowed Mowital replica.

20,000X



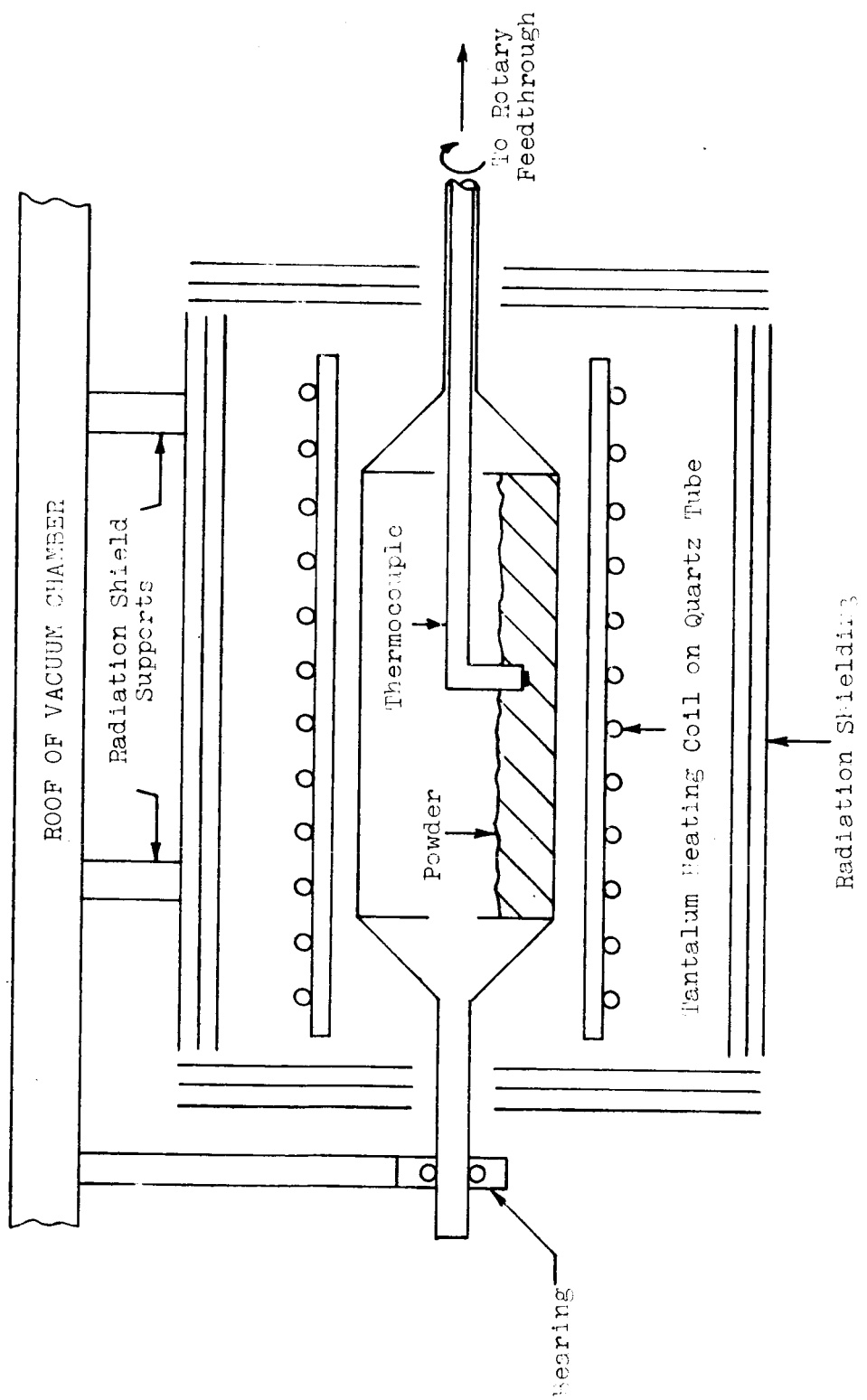


Figure 7 The furnace system used in the ultrahigh vacuum chamber.



Figure 8

Stainless steel rotating device for powder treatment in a continuously pumped vacuum system, which is shown in the background.

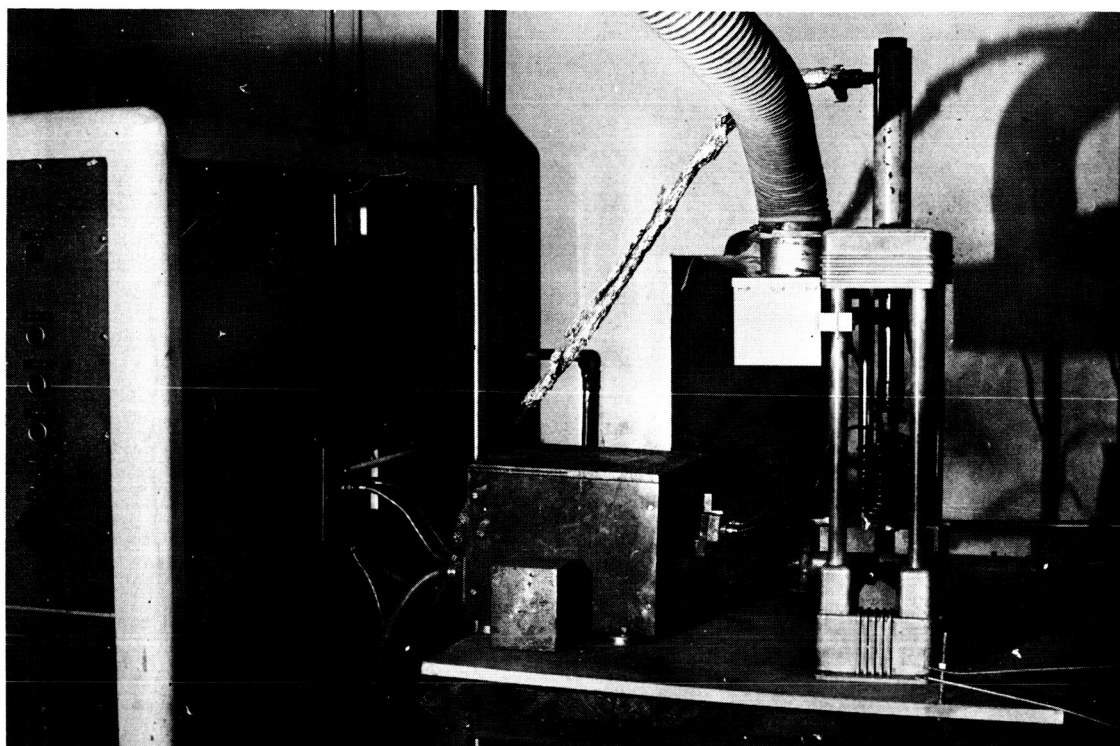


Figure 9

Induction furnace for hot pressing  
treated powders.

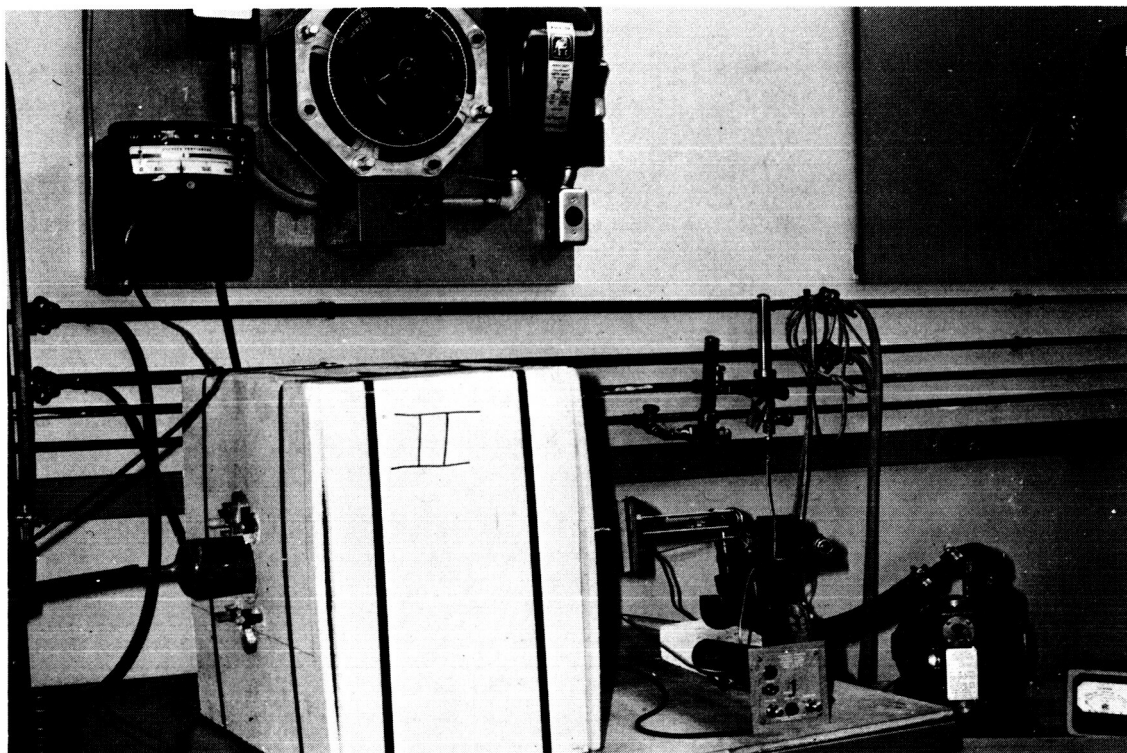


Figure 10

Quartz tube furnace used for treating  
intermediate and final series of powders.

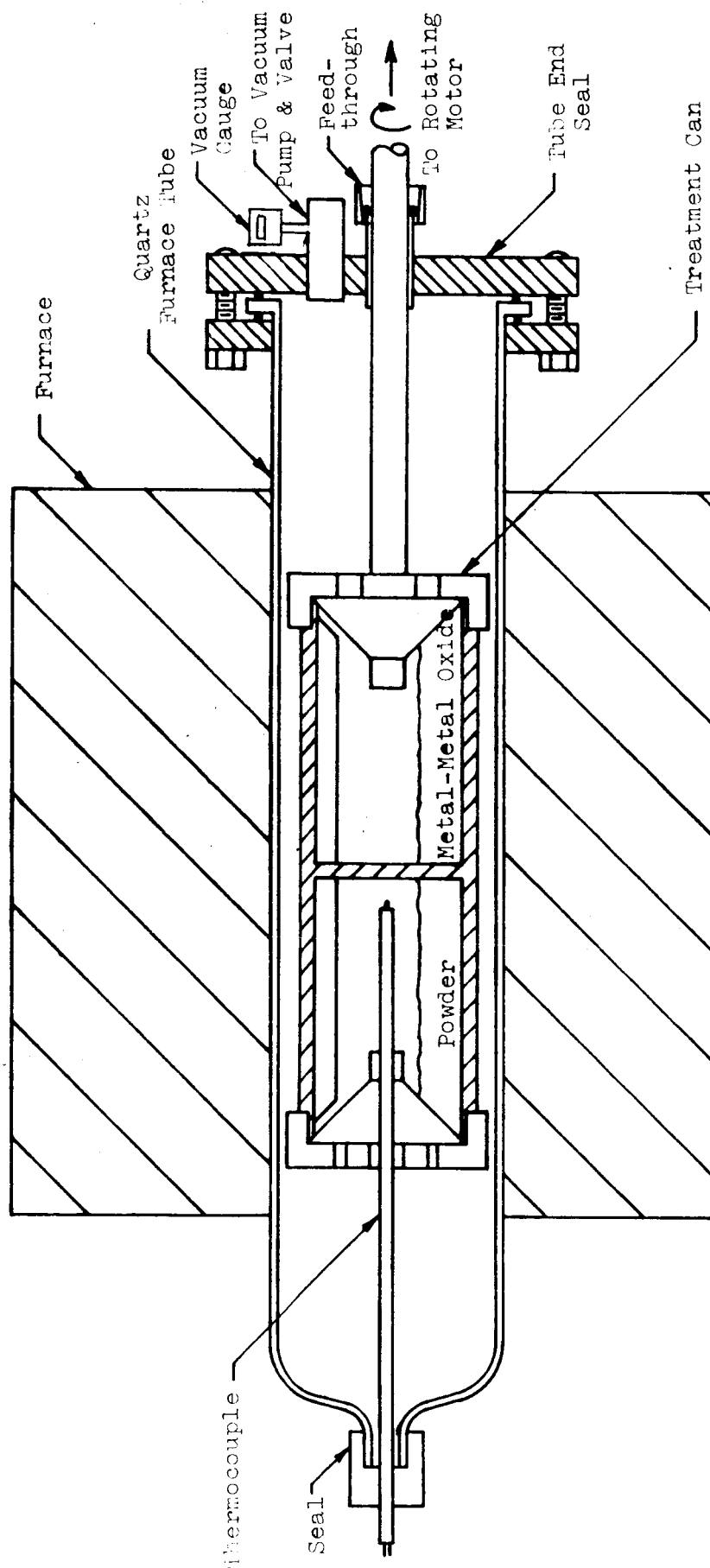


Figure 11 Cut-away drawing of the quartz tube furnace used in the intermediate and final series of treatments.

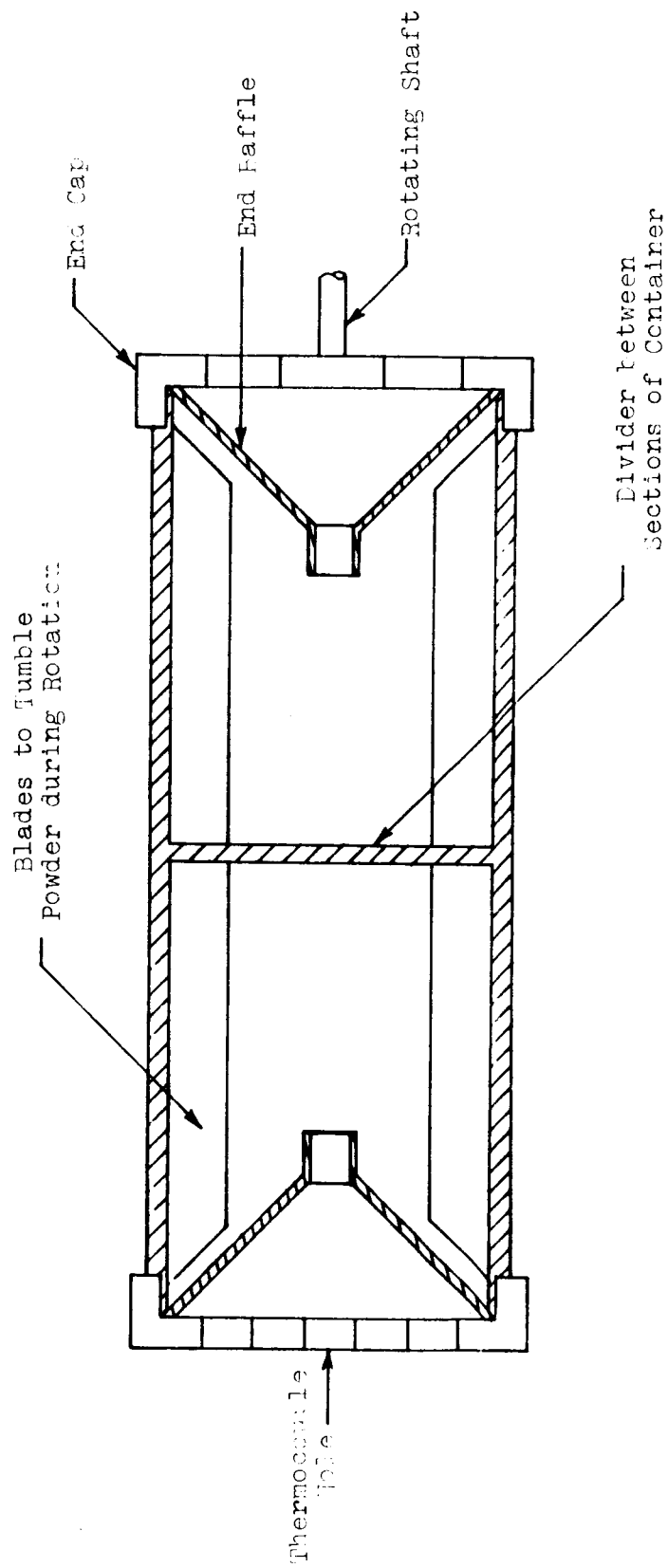


Figure 12. Stainless steel container used during powder treatments in the quartz tube furnace.

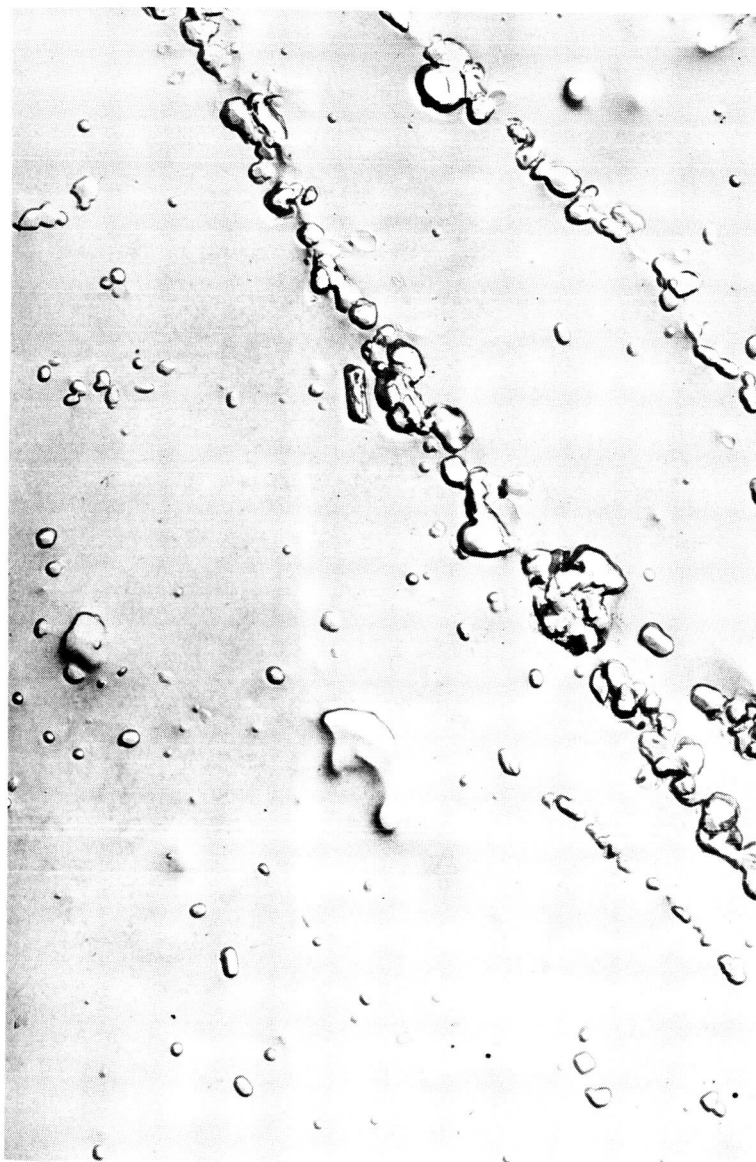


Figure 13

Typical particle distribution obtained in the intermediate series of treatments in Ni-NiO atmosphere. Heavy oxidation can be seen in the two interpowder particle boundaries in the top right-hand corner. Ge shadowed, 2 stage carbon replica.

8000X

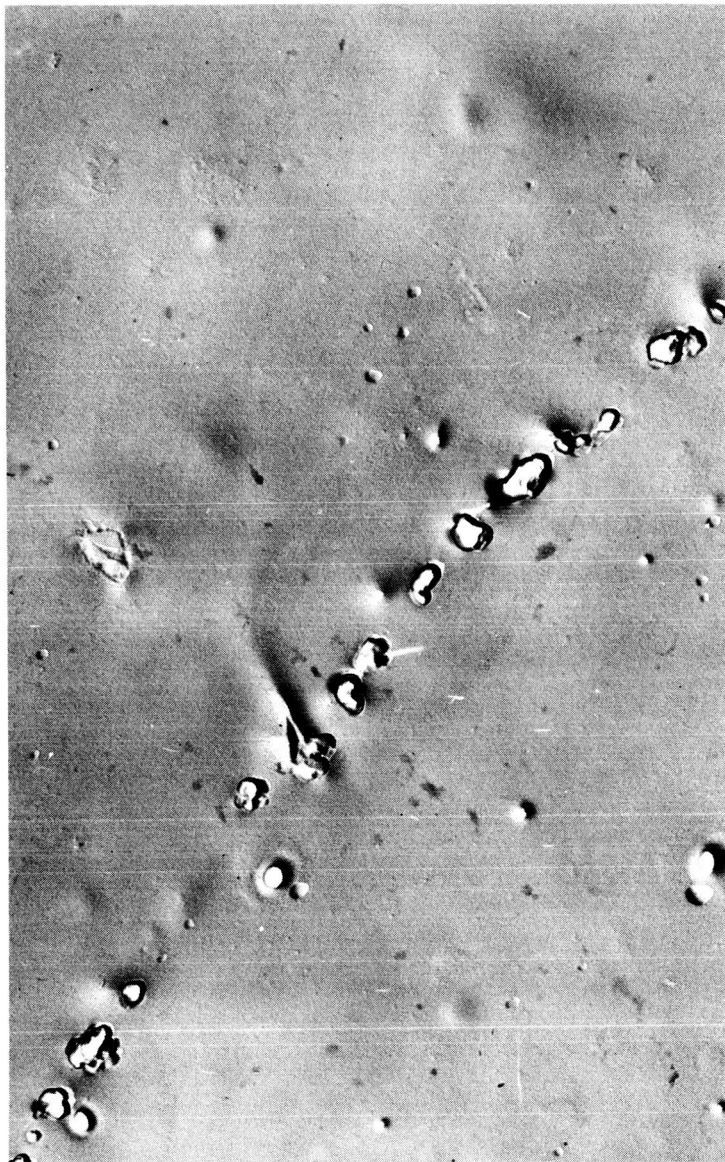


Figure 14

Particle distribution typical of that obtained in the final series of treatments carried out for 48 hours at 700°C, or 24 hours at 750°C, as shown in Specimen D, Alloy I. The oxide is restricted to the powder particle boundary. Ge shadowed, 2 stage carbon replica.

10,500X





Figure 15

Particle distribution typical of that obtained in the final series of treatments carried out for 48 hours at  $750^{\circ}\text{C}$ , or 24 hours at  $800^{\circ}\text{C}$ , as shown in Specimen C, Alloy III. Ge shadowed, 2 stage carbon replica. 10,500X

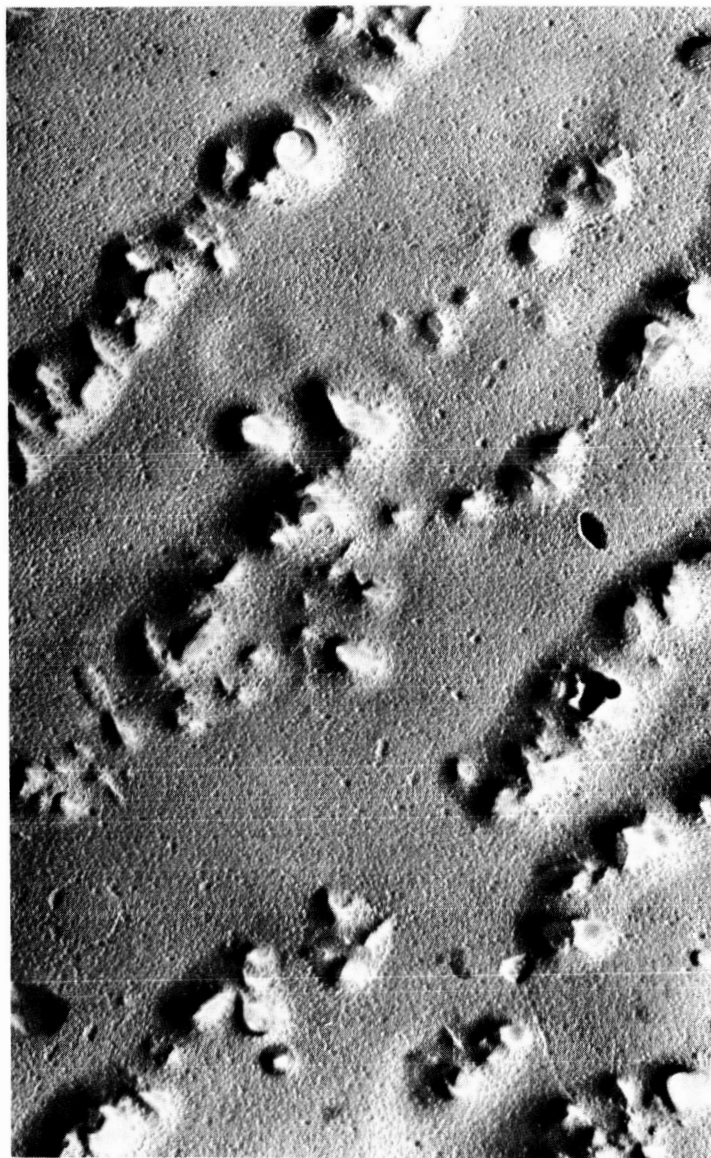


Figure 16

Particle distribution typical of that obtained in the final series of treatments by increasing the oxygen available to the powder, as shown in Specimen Z, Alloy III. Ge shadowed, 2 stage carbon replica.

23,700X



Figure 17

Electron micrograph of compacted powder (Alloy III) showing  $\gamma'$  particles which form at boundaries. The large number of small round objects with shadowing tails are Latex balls used for magnification checks. Ge shadowed, 2 stage carbon replica. 12,000X

## APPENDIX A

### Calculation of Interparticle Spacing Using Program Guidelines\*

1) volume fraction =  $\frac{\# \text{ of particles}}{\text{unit volume}}$  x volume of each particle

$$f = N \times \frac{4}{3} \pi r^3$$

where  $0.02 < f < 0.08$

$0.05 \mu < r < 0.15 \mu$

2) solving for particle density, N, at the extreme cases;

a) where f is large, r is small, maximum value of N  
and

b) where f is small, r is large, minimum value of N

a) maximum value of N

$$N = \frac{f}{\frac{4}{3} \pi r^3}$$

$$N = \frac{0.08}{(\frac{4}{3})(\pi)(0.05 \mu)^3} = \frac{0.08}{(\frac{4}{3})(\pi)(1.25 \times 10^{-16} \text{cm}^3)}$$

$$N = \frac{0.08}{5.24 \times 10^{-16} \text{cm}^3} = \frac{1.53 \times 10^{+14}}{\text{cm}^3}$$

b) minimum value of N

$$N = \frac{f}{\frac{4}{3} \pi r^3}$$

$$N = \frac{0.02}{(\frac{4}{3})(\pi)(0.15 \mu)^3} = \frac{0.02}{(\frac{4}{3})(\pi)(3.38 \times 10^{-15} \text{cm}^3)}$$

$$N = \frac{0.02}{1.42 \times 10^{-14} \text{cm}^3} = \frac{1.4 \times 10^{+12}}{\text{cm}^3}$$

\* Sample calculation based on Figure 17.

3) center-to-center spacing,  $\lambda$

$$\left(\frac{1}{\lambda}\right)^3 \approx N$$

$$\lambda \approx N^{-1/3}$$

a) minimum value of  $\lambda$  (corresponds to maximum N)

$$\lambda = \left( \frac{1.53 \times 10^{14}}{\text{cm}^3} \right)^{-1/3}$$

$$\lambda = \frac{1 \text{ cm}}{5.35 \times 10^{+4}} = 1.87 \times 10^{-5} \text{ cm}$$

b) maximum value of  $\lambda$  (corresponds to minimum N)

$$\lambda = \left( \frac{1.4 \times 10^{12}}{\text{cm}^3} \right)^{-1/3}$$

$$\lambda = \frac{1 \text{ cm}}{1.11 \times 10^4} = 9.1 \times 10^{-5} \text{ cm}$$

or:

$$0.187 \mu < \lambda < 0.9 \mu$$

4) interparticle spacing,  $L = \lambda - d$

$$0.087 \mu < L < 0.6 \mu$$